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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 8/00, 290/00, C09D 5/03	A1	(11) International Publication Number: WO 97/46594 (43) International Publication Date: 11 December 1997 (11.12.97)
(21) International Application Number: PCT/EP97/02774 (22) International Filing Date: 24 May 1997 (24.05.97) (30) Priority Data: MI96A001097 30 May 1996 (30.05.96) IT (71) Applicant (for all designated States except US): VIANOVA RESINS S.P.A. [IT/IT]; Via Matteo Bianchin, 62, I-36060 Romano D'Ezzelino (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): FARRONATO, Silvestro [IT/IT]; Via Don Sturzo, 43, I-36060 Romano D'Ezzelino (IT). GAZZEA, Sergio [IT/IT]; Via Raffaello Sanzio, 13, I-36060 Romano D'Ezzelino (IT). CHINELLATO, Roberto [IT/IT]; Via Orobani, 5, I-30175 Venezia-Marghera (IT). (74) Agent: RICCARDI, Sergio; Riccardi & Co., Via M. Melloni, 32, I-20129 Milano (IT).		(81) Designated States: AU, CA, JP, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR THE SYNTHESIS OF RESINS CONTAINING UNSATURATIONS OF THE (METH)ACRYLIC TYPE TO BE CURED BY RADIATION OR HEAT AND USED FOR POWDER PAINTS (57) Abstract This invention is characterized by the fact that resins comprising (meth)acrylic unsaturations are obtained by reacting functional groups of unsaturated monomers without solvents at temperatures above 150 °C and under controlled heat exchange, while maintaining intact their unsaturations, with functional groups of saturated and/or unsaturated polymers. The technologies and the work cycles used for conventional resins may also be used for these resin types.		

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**"PROCESS FOR THE SYNTHESIS OF RESINS CONTAINING
UNSATURATIONS OF THE (METH)ACRYLIC TYPE TO BE CURED BY
RADIATION OR HEAT AND USED FOR POWDER PAINTS"**

5 [Description]

Owing to known strong homopolymerization tendency of acrylic monomers in order to yield polymers comprising acrylic unsaturations, relatively low temperatures are used (in the range of 60 to 130°C; at most 150°C) together with suitable amounts of polymerization inhibitors and by adding solvent in order to lower polymer viscosity. In
10 this way, uniform mass heating is favoured and local superheating, which would cause the polymerization of unsaturated functionalities, is avoided.

Several processes, working either in the presence of solvents or at relatively low temperatures together with short reaction times to yield polymers comprising unsaturated groups for powder paints, are known.

15 EP 0249306 (Autotype Int.Appl.)discloses an unsaturated polymer obtained in toluene solution wherefrom it is precipitated and filtered. EP 0636669 and EP 0644905 (DSM) disclose polymers obtained at temperatures of 50 to 110°C in butylacetate solution or toluene/xylene solution followed by solvent stripping at 150°C. EP 0650978 (BASF) discloses unsaturated polymers obtained without solvents, but homogenized by
20 extruding reactive compounds together with unsaturated functional monomers at temperatures up to 130°C for a short time (7-15 min).

These limitations in temperatures and time impair the possibility of using the synthesis. However, many manufactures of resins for powder paint are in the need of carrying on, also for these types of resins, the use of technologies and work cycles used
25 for conventional resins such as polyesters and acrylics, which are manufactured at temperatures above 150°C, up to 260°C, and unloaded at temperatures between 160 and 220°C for a relatively long time (0,5-8 hours) dependent upon the resin amount and the crushing rate of the flaking machine. However, for the above stated reasons, that has not been possible up to now.

30 It has now surprisingly been found possible to add an unsaturated functional monomer to a resin comprising reactive functional groups, maintained at temperatures in the range of 150°C to 200°C and with an addition of suitable inhibitor amounts, and to react it with the resin for 50 to 60 minutes without affecting the resin unsaturation.

This object is achieved by supplying the reaction mass with heat in order to avoid local superheating. This in practice occurs by maintaining the temperature in the range of values reached during the exothermic reaction or slightly higher without the need of adding solvents.

5 Starting polymers usable for the purposes of this invention may be either acrylic resins or saturated or unsaturated polyesters having reactive groups such as hydroxy, carboxylic, glycidil, isocyanate groups, whereas (meth)acrilics comprising functional groups mentioned above are especially used as reactive monomers.

10 The unsaturated functional monomers are preferably selected from the group consisting of glycidil(meth)acrylate, (meth)acrylic acid, methacrylisocyanate, benzo-1-(1-isocyanate-1-methyl)-4,1-methenyl, isocyanateethylmethacrylate or unsaturated isocyanate adducts.

15 Polymerization inhibitors are conventional inhibitors such as hydroquinone, hydroquinone-monomethylether, mono-ter-butylhydroquinone, phenotiazine, diethylhydroxylamine, diphenyl-p-phenylenediamine, isopropyl-phenyl-p-phenylenediamine, triphenylphosphite.

The process of this invention will now be described, but not limited by the following examples, wherein the term "parts" is to be intended as "parts by weight".

Example 1

20 In a four-neck flask provided with a thermometer, a stirrer, a distillation column and an inert gas bubbling inlet, 1500 parts of Alftalat AN 725 (carboxylic polyester provided by Hoechst and having NA=30-36, cone-plate viscosity of 4000-7000 mPas/200°C, Tg = 63-69°C) were loaded. The resin was melted at 180°C and thereafter 250 parts of glycidil methacrylate together with 1 part of hydroquinone were added
25 dropwise and under stirring for 20 minutes. This temperature was maintained through mild heating until NA=3 and cone-plate viscosity of 1120 mPas/200°C were reached. Thereafter the temperature was brought to 170°C and the mass was maintained at this temperature for 3 hours without having gelation followed by its unloading and its cooling. The obtained product had NA=1.5 and cone-plate viscosity of 1680 mPas/200°C,
30 Tg = 40°C and equivalent weight unsaturation grade of about 1000.

Example 2

Following the same process of Example 1 850 parts of Synthacryl VSC 1438 (glycidil resin provided by Hoechst and having EEW = 360-400, cone-plate viscosity of 8000-

12000 mPas/170°C, $T_g = 46-52^\circ\text{C}$), were loaded and after having melted the mass at 180°C, 2.5 parts of triphenylphosphite, 8 parts of hydroquinone and 1 parts of phenothiazine were added. After homogenization of the resultant mass 150 parts of methacrylic acid were added dropwise for 10 min. After 10 minutes from the conclusion of the addition, the final product was examined and it was found to have NA = 1 and cone-plate viscosity of 2600mPas/200°C. The temperature of 180°C was maintained for another hour and after this time the mass was unloaded. The obtained product was found to have NA = 0.5, cone-plate viscosity of 3400 mPas/200°C, softening point of 80-85°C, equivalent weight unsaturation grade of about 575.

Example 3

In a 5 liter reactor provided with a thermometer, a stirrer and an inert gas bubbling inlet 620 parts of ethyleneglycol, 150 parts of neopentylenglycol, 1328 parts of terephthalic acid and 2 parts of monobutylstannic acid were loaded. Therefore the mass was heated at 240°C in order to obtain hydroxy saturated polyester having NOH of about 200. The polyester was cooled at 170°C and 441 parts of maleic anhydride and 0.4 parts of hydroquinone were added, followed by heating at 200°C until an unsaturated polyester having NA = 50, cone-plate viscosity of 1440 mPas/200°C and softening point of 80-85°C was obtained. Thereafter the product was cooled at 180°C and at this temperature 300 parts of glycidilmethacrylate together with 1 part of hydroquinone were added for 10 min. After 15 minutes the product was examined and it was found to have NA = 0.8 and cone-plate viscosity of 1000 mPas/200°C. The mass was maintained at 180°C for further 8 hours and after its cooling the product had NA = 0.8, cone-plate viscosity of 1320 mPas/200°C, softening point of 80-85°C and equivalent weight unsaturation grade of about 380.

Example 4

In a 5 l reactor provided with a thermometer, a stirrer, a distillation column and an inert gas bubbling inlet 1507 parts of 1,4-butanediol, 2098 parts of fumaric acid and 2.7 parts of monobutylstannic acid were loaded. Therefore the mass was heated at 120°C in order to obtain an unsaturated polyester having NA = 108 and cone-plate viscosity of 160 mPas/200°C and after cooling at 170°C, 1.4 parts of hydroquinone and 388 parts of glycidilmethacrylate were added. After 10 minutes the product was examined and it was found to have NA = 51 and cone-plate viscosity of 160-200°C. The mass was maintained at 170°C for further 4 hours and after this time the product was

unloaded and an unsaturated crystalline polymer having MP of 75-80, cone-plate viscosity of 140 mPas/200°C, NA = 41 and unsaturated equivalent weight of about 90, was obtained.

Example 5

5 In a 5 l reactor provided with a thermometer, a stirrer and a reflux condenser 320 parts of dimethylmaleate were loaded and the mass was heated at 150°C. Thereafter a blend consisting of 880 parts of styrene, 100 parts of methacrylic acid, 440 parts of methylmethacrylate, 300 parts of butylacrylate and 20 parts of di-ter-amyl peroxyde was added dropwise for 6 hours. After the addition was completed the product was maintained
10 at 170 °C for 1 hour and then brought under vacuum until a solid residue >95%, NA= 31.6, cone-plate viscosity of 21120 mPas/200°C and Tg = 55°C, were obtained. Then 4 parts of triphenylphosphite, 10 parts of hydroquinone and 1 part of phenotiazine were loaded. After homogenization 180 parts of glycidilmethacrylate were added for 10 minutes. The product was maintained at 170°C and after 1 hour it was found to have NA
15 = 7 and cone-plate viscosity of 7040 mPas/200°C. After further 2 hours at 170°C the product was unloaded and cooled. It was found to have NA = 2, cone-plate viscosity of 800 mPas/200°C, Tg = 44°C.

Application tests

1. UV hardening

20 The resins produced in the above examples were used according to the following composition for powder paint by using UV-rays hardening:

Resin : 92%

Flow promoter* 5%

UV photoinitiator 3%

25 * Master Additol XL 496 (hydroxy EW 85% + polyacrylate 15%)

The paint composition comprising the resin of the example 2 contains LH 746 (polyurethaneacrylate provided by Hoechst) as co-crosslinking agent with a resin/co-crosslinking agent ratio corresponding to 70/30.

30 A twin screw extruder was used for these application tests under the following conditions:

Temperature zone (°C): 80-100-100

Feed (%): 20

Rotation speed (rpm): 300

The obtained paints were applied by using a corona gun and the film was hardened on a dynamic UV-IR oven provided with ten IR 230V/800W lamps and two 80 W/cm UV lamps.

For the acceptance tests Al metal sheets and MDF wooden panels were used.

5 Acceptance test results:

Properties	Example 1	Example 2	Example 3	Example 4	Example 5
acetone resistance	3	2	1	3	5
10 24h stability at 35°C	2-3	2-3	5	1-2	5
15 impact test on MDF panel Joule	14	<6	10	<6	<6

5: negative 4: insufficient 3: sufficient 2: moderate 1: good

2. IR hardening

20 By using Perkadox SB as thermic initiator, the resin of the example 5 showed a gelation time corresponding to 58 s at 180°C. The same initiator was used to examine the resin of the Example 3 with the following composition:

Resin : 92%

Flow promoter 5%

IR catalyst 3%

25 The extrusion conditions were the same as the above stated ones. The crosslinking conditions corresponded to a single passage through the IR lamps area at 0.5m/min. Acetone resistance resulted moderate.

Claims

1. Process for making the synthesis of resins comprising hardenable (meth)acrylic unsaturations by means of radiations or heat characterized in that said resins are obtained by reacting:

5 a. saturated and/or unsaturated polymers or polycondensates comprising one or more reactive functional groups per molecule;

 b. unsaturated monomers comprising a functional group which is able to react with functional groups of said polymers or polycondensates,

10 at a temperature above 150°C without solvents, in the presence of polymerization inhibitors and under thermic heat exchange.

2. Process according to Claim 1 characterized in that the polymers and the polycondensates are selected from the group consisting of acrylic resins, saturated polyesters, unsaturated polyesters, vinyl resins and epoxy resins.

15 3. Process according to Claims 1 and 2 characterized in that as reactive groups the polymers and the polycondensates comprise hydroxy, carboxylic, anhydride, glycidil and isocyanate groups.

4. Process according to Claim 1 characterized in that the unsaturated monomers are (meth)acrylates comprising hydroxy, carboxylic, anhydride, glycidil and isocyanate groups as functional groups.

20 5. Process according to Claims 1 and 4 characterized in that the unsaturated monomers are selected from the group consisting of glycidil(meth)acrylate, (meth)acrylic acid, methacrylisocyanate, benzo-1-(1-isocyanate-1-methyl)-4,1-methenyl, isocyanateethylmethacrylate or unsaturated isocyanate adducts.

6. Resins obtained by the process according to Claims 1 to 5.

25 7. Compositions for powder paint, self-crosslinking or co-crosslinking by means of UV radiations or heat, characterized in that they comprise the resins according to Claims 1 to 6.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/02774

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F8/00 C08F290/00 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

9 October 1997

Date of mailing of the international search report

24. 10. 97

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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